

Morphology, optical properties and single-electron spectrum of 'detector-quality' DLC layers, prepared by MW CVD

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So-called 'charge collection distance' rises apparently at the increment in the film thickness and average grain size in 'detector-quality' polycrystalline DLC films [1]. This effect was mainly attributed to diminishment in density of inter-granular defects in thicker DLC films with bigger average grain sizes, whereas density $N(E)$ of the 'in-grain' states was supposed to be independent on the film thickness and morphology. In our study we are intend to demonstrate, that the $N(E)$ distribution for the intra-granular electron states could also be influenced considerably by sizes of the DLC grains. Dependencies of spectrum of coefficient of optical absorptions, $\alpha(h\nu)$, 'indirect' gap width E_G and Urbach tail slope E_U of freestanding polycrystalline diamond-like carbon (DLC) films on their thickness and morphology have been studied. Two series of the $\langle 100 \rangle$ - and $\langle 110 \rangle$ -oriented DLC samples with different thickness were initially grown on the $\langle 100 \rangle$ -oriented silicon substrates by microwave plasma chemical vapour deposition (MW CVD) at fixed (within each series) deposition conditions, and thereafter separated from the silicon substrates. Main deposition and morphological parameters of the studied films are given in the Table.

Sample series	T_s , °C	Gas mixture	Dominant crystalline orientation	Thickness range, μm	Average grain size, μm
'a'	670	$\text{H}_2:\text{CH}_4:\text{O}_2$ 400:8:2	$\langle 100 \rangle$	2.0 – 20.0	0.4 – 4.0
'b'	670	$\text{H}_2:\text{CH}_4:\text{CO}$ 400:5:10	$\langle 110 \rangle$	3.0 – 12.0	0.8 – 3.1

Alteration in crystalline orientation of the DLC layers has been achieved via changes in composition of a gas mixture employed at the samples depositions (see the Table) as well as by implementing of a short period of pure hydrogen plasma etching immediately after the nucleation process.

An increment in the film thickness from 2 to 20 μm for $\langle 100 \rangle$ -oriented samples and from 3 to 12 μm for the $\langle 110 \rangle$ -oriented ones cause almost linear enlargement in the average transverse size of the surface morphology (from 0.4 to 4.0 μm for the $\langle 100 \rangle$ -oriented samples and from 0.8 to 3.1 μm at the $\langle 110 \rangle$ -oriented ones), see the Table. At the same time, significant lowering in the $\alpha(h\nu)$ (Fig.1, symbols) and E_U values (the E_U drops from 615 ± 15 to 299 ± 4 meV) is observed as thickness of the DLC samples rises, while the E_G quantity remains almost constant and equals to 5.40 ± 0.05 eV for the all studied samples. Such abnormal $\alpha(h\nu)$ and E_U dependencies on the film thickness are attributed to significant influence of average sizes of DLC grains on the $N(E)$ parameters within and just beyond the band gap of the material. A simulation of the influences of the granular morphology on the $\alpha(h\nu)$ and $N(E)$ spectra of the DLC has been fulfilled within a framework of semi-empirical adiabatic Generalized Skettrup Model, GSM [2-4]. The GSM is essentially based on statistical description of behaviour of multiple acoustic phonons, confined within volumes of the DLC grains. It also employs assumptions on linear relationship in between single-electron energy E and reduced elastic energy of this material as well as on absence of momentum conservation for all optically activated carrier transitions. The $N(E)$ distribution within framework of the GSM is predetermined by formulas:

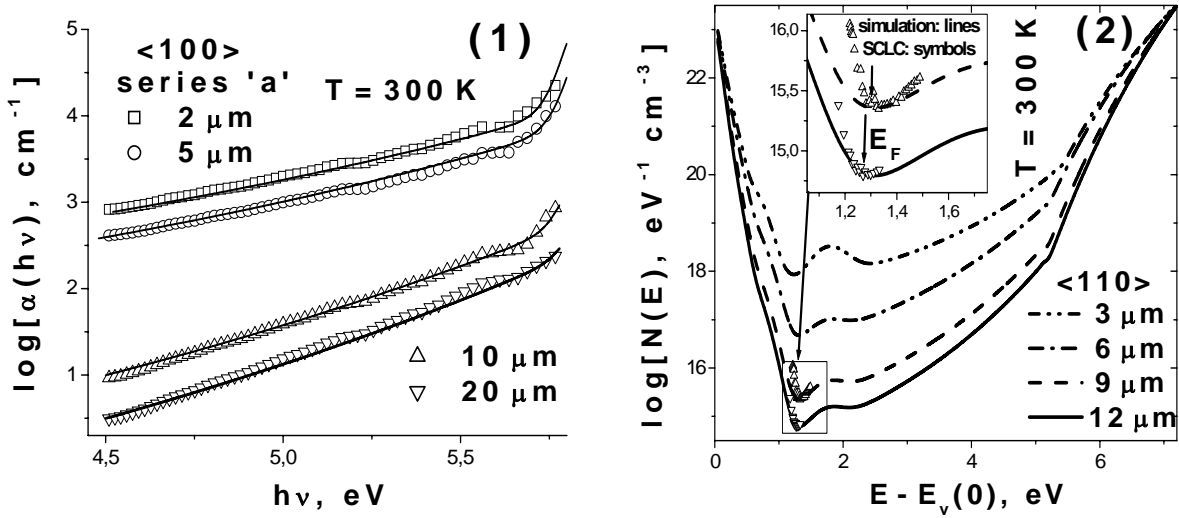
$$N_c(E) = \frac{ZD}{B_c} W_c[E_G(0,0) - E] \quad (1a); \quad N_v(E) = \frac{ZD}{B_v} W_v(E), \quad (1b).$$

$$W_{c,v}(E) \cong \exp\left(-\frac{E}{k_B T_{c,v}}\right) \int_0^\infty \frac{1}{Z_M [\Gamma(M)]^{r1}} \left[\frac{2L_x L_y F(L_x, L_y, L_z) E^2}{M^{r2} (B_{c,v} hc_s)^2} \right]^M dM, \quad (2)$$

where D is an average atomic density, Z is the atomic valency, B_v and B_c are dimensionless constants which characterize the intensity of interactions of the confined acoustic phonons with charge carriers on bonding (within the VB) and anti-bonding (within the CB) electron levels, respectively; ZQE/B is an instant value of aggregate

energy of *all* longitudinal acoustic phonons, confined at the given moment in time in a rectangular coherency cell with orthogonal edges of the lengths L_x , L_y , L_z , Q is the number of atoms (of a single sort) in the confinement volume ($Q \equiv D * L_x * L_y * L_z$), $M = N/ZQ$ and $M0 = N0/ZQ$, $N0$ is the integer *ceil* of the $ZQE/Bk_B\theta_D$ ratio (here *ceil* denotes the smallest integer greater than or equal to the rational quantity in the brackets), T and θ_D are the absolute and Debye temperatures (respectively), k_B is the Boltzmann constant, $\Gamma(M)$ is the Euler gamma-function, c_s is a velocity of longitudinal sound waves, Z_M is a statistical sum, and $r1$ and $r2$ are model parameters ($1 \leq r1 \leq 0.5$; $2 \leq r2 \leq 0.5$) [4]. The function $F(L_x, L_y, L_z)$ in Eq.(2) depends only on the ratios of the edge lengths [4]. The $E_G(0, 0) = 7.216$ eV, and $N(E)$ equal to $N(E)_v + N(E)_c$.

This model reproduces experimentally observed changes in the parameters of both ‘algebraic’ and exponential parts on the optical absorption spectrum, which occur at alterations of the thickness and average grain sizes of the studied DLC samples (Fig. 1, lines). All $\alpha(h\nu)$ curves in this figure have been simulated at varied lengths L_x , L_y , L_z of the phonon confinement, but almost constant values of other simulation parameters (c_s , B_c , B_v , D , $E_G(0)$, T , Z and θ_D). In particular, each of the L_x , L_y , L_z dimension is assumed to be exactly equal to the average transverse size of the DLC grains, deduced from the SEM image of the given sample. The model parameters $r1$ and $r2$ have also been slightly varied in the $0.820 \leq r1 \leq 0.845$ and $0.710 < r2 < 0.740$ ranges in order to obtain the best approximation of the simulation curves for the experimental data. The GSM allows us to explain as well an existence of Urbach tail with relatively large E_U values in high-quality polycrystalline DLC films and diamond powder with ordered atomic structure within DLC/powder grains. Fig. 2 reveal the $N(E)$ curves, simulated for the films from the ‘b’ series at the above-listed values of the GSM parameters. These simulation results are in reasonable quantitative agreement with the experimental data on the defect states density in the $\langle 110 \rangle$ -oriented films, obtained with the space-charge-limited-current technique [5], see insertion in Fig. 2.



Figs. 1, 2. Typical experimental (symbols) and simulated (lines) (1) $\alpha(h\nu)$ and (2) $N(E)$ spectra of the DLC.

References

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